# Dispersion and Thermal Stability of MoO$_3$ on TiO$_2$-ZrO$_2$ Mixed Oxide Support

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**TiO$_2$-ZrO$_2$ mixed oxide support containing 1 : 1 mole ratio was prepared by the coprecipitation method and impregnated with MoO$_3$. Ammonium heptamolybdate was used as source of MoO$_3$, and molybdena contents were varied from 2 to 12 wt%. The TiO$_2$-ZrO$_2$ support and MoO$_3$/TiO$_2$-ZrO$_2$ catalysts were subjected to thermal treatments from 773 to 1073 K and were investigated by X-ray diffraction, FT-infrared, oxygen uptake, and BET surface area measurements to establish the effects of molybdena loading and thermal treatments on the surface structure of dispersed molybdena species and thermal stability of the catalysts. Calcination of Ti- and Zr-hydroxides at 773 K result in the formation of an amorphous phase, and further heating to 973 K produces a crystalline ZrTiO$_4$ compound. This compound is quite stable even up to 1273 K in the absence of MoO$_3$. Impregnation of MoO$_3$ and heating of the samples result in the formation of the ZrMo$_2$O$_8$ compound. This compound is highly sensitive to the concentration of MoO$_3$ and calcination temperature.** © 1998 Academic Press

## INTRODUCTION

Over the past years a great deal of fundamental and applied research was focused on supported molybdena catalysts because of their numerous applications in petroleum refining, chemicals production, and pollution control industries (1–3). Presently, oxidation reactions are playing an increasingly important role, both in the production of materials needed and in the destruction of undesired products by total catalytic oxidation. Supported and unsupported molybdates are among the most successful oxidation and ammoxidation catalysts (4–8). A renewed interest arose recently in the supported molybdena catalysts owing to their potential use in the partial oxidation of methane to formaldehyde (9,10).

Until recently most of the research work was focused on alumina-supported molybdena catalysts. Supports other than alumina, e.g., titania, titania-silica, titania-alumina, zirconia, titania-zirconia, or carbon have received less attention (11–14). Titania (anatase) is a preferred support for

Mo-based catalysts for selective catalytic reduction (SCR) of nitrogen oxides and it has also been found to exhibit favorable properties when used as a support for sulfided Mo-based catalysts for hydrodesulfurization of thiophenic compounds (15,16). The successful role of TiO$_2$ (anatase) as a support material to MoO$_3$ is owing to the formation of layer structure of MoO$_3$ on TiO$_2$ due to crystallographic fittings of (110) and (010) planes of MoO$_3$ with (010) and (001) planes of anatase (17). Zirconia is yet another interesting support as well as catalyst (18). Sulfided MoO$_3$/ZrO$_2$ catalyst was found to exhibit excellent catalytic properties for hydrodesulfurization of thiophene despite its typically small surface area (11). The inherent favorable characteristics of both titania and zirconia supports can be explored fully by using them in combination with each other. Therefore, the combined TiO$_2$-ZrO$_2$ mixed oxide has attracted the attention recently as a catalyst and as a support for various applications. For example, recent studies reveal that the TiO$_2$-ZrO$_2$ is an active catalyst for dehydrocyclization of *n*-paraffins to aromatics (19) and hydrogenation of carboxylic acids to alcohols (20), and as a support for MoO$_3$-based catalysts for hydroprocessing applications (21).

The aim of the present study is to provide basic insights into the surface structure of MoO$_3$/TiO$_2$-ZrO$_2$ catalysts, shedding light on the influence of thermal treatments, oxide loading, and preparation method on both thermal stability and chemisorption properties of this catalyst system. Temperature stability in catalysis is of vital importance, since in high temperature oxidations or SCR, long-term thermal stability dictates the catalyst life. In this investigation temperature effects are examined by different characterization techniques including XRD, FTIR, oxygen chemisorption, and BET surface area measurements.

## EXPERIMENTAL

### Catalyst Preparation

The TiO$_2$-ZrO$_2$ mixed oxide (1 : 1 mole ratio) support was prepared by a homogeneous coprecipitation method using urea as precipitation reagent (22). An aqueous mixture

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solution containing the requisite quantities of $TiCl_4$ (Fluka, AR grade), $ZrOCl_2$ (Fluka, AR grade), and urea (Loba Chemie, GR grade) were heated together to 368 K with vigorous stirring. In about 6 h of heating, as decomposition of urea progressed to a certain extent, the formation of precipitate gradually occurred and the pH of the solution increased. The precipitate was heated for six more hours to facilitate aging. The coprecipitate was then filtered off, washed several times with deionized water until free from chloride ions, and dried at 393 K for 12 h. The oven-dried precipitate was finally calcined at 773 K for 6 h in open-air atmosphere. The resulting $TiO_2$-$ZrO_2$ mixed support had a $N_2$ BET surface area of 160 $m^2g^{-1}$ and was found to be uniform throughout the bulk. Some portions of this support were once again heated at 873, 973, 1073, and 1273 K for 6 h in a closed electrical furnace in open-air atmosphere.

The $MoO_3$/$TiO_2$-$ZrO_2$ catalysts, containing 2 to 12 wt% $MoO_3$ were prepared by a standard wet impregnation method. To impregnate $MoO_3$, the requisite quantity of ammonium heptamolybdate (JT Baker, England, AR grade) was dissolved in doubly distilled water and pH of the solution was brought to 8–8.5 by adding few drops of dilute ammonia, and the finely powdered calcined (773 K) mixed oxide support was added to this solution. The excess water was evaporated on a water bath with continuous stirring. The resultant solid was then dried at 383 K for 12 h and calcined at 773 K for 6 h in a closed electrical furnace in open-air atmosphere. Some portions of the finished catalysts were once again heated at 873, 973, 1073, and 1273 K for 6 h in a closed electrical furnace in open-air atmosphere. The rate of heating (as well as cooling) was always maintained at 10 K $min^{-1}$.

### Catalyst Characterization

*X-ray diffraction.* X-ray powder diffraction patterns have been recorded on a Siemens D-500 diffractometer by using CuK$_\alpha$ radiation source and Scintillation Counter detector. The XRD phases present in the samples were identified with the help of ASTM Powder Data Files.

*Infrared spectra.* The FTIR spectra were recorded on a Nicolet 740 FTIR spectrometer at ambient conditions, using KBr discs, with a nominal resolution of 4 $cm^{-1}$ and averaging 100 spectra.

*Chemisorption measurements.* A conventional standard volumetric high vacuum ($1 \times 10^{-6}$ Torr) system with the facility for reducing the samples *in situ* by flowing purified hydrogen (35 $cm^3$ $min^{-1}$) was used for high temperature (643 K) oxygen chemisorption (HTOC) measurements. Catalyst samples (ca 0.5 g) were reduced for 4 h at 643 K followed by evacuation ($1 \times 10^{-6}$ Torr) at the same temperature for 2 h. The amount of oxygen chemisorbed was then determined as the difference between the two successive adsorptions generated at 643 K. In between the first

and second adsorption isotherms, the sample was evacuated for 1 h at the same adsorption temperature. More details of this method are described elsewhere (23). The BET surface area of the catalyst was determined by $N_2$ physisorption at 77 K by taking 0.162 $nm^2$ as the area of cross section of $N_2$ molecule.

## RESULTS AND DISCUSSION

The quantity of $MoO_3$ required for covering the $TiO_2$-$ZrO_2$ support surface (BET SA 160 $m^2g^{-1}$) as a monomolecular layer can be estimated from theoretical means. As reported by Hengstun *et al.* (24), theoretically a load of 0.16 wt% per $m^2$ of support surface is required in order to cover the support surface as a compact single lamella of molybdenum oxide structure. However, Bond *et al.* (25), Baiker *et al.* (26), and Haber *et al.* (27) experimentally observed that the actual loading required to cover the $TiO_2$ surface as a single monolayer was always less than the theoretical value and corresponds to about 70% of theoretical estimation. Kim *et al.* (28) recently reported that for Degussa P-25 $TiO_2$ support, the required quantity of $V_2O_5$ or $MoO_3$ is 0.12 wt%. In view of these reasons a range of molybdenum oxide compositions were selected from 2–12 wt% in the present investigation.

The XRD patterns of the $TiO_2$-$ZrO_2$ support (1:1) calcined at various temperatures from 773 to 1273 K are shown in Fig. 1. As can be noted from this figure, the $TiO_2$-$ZrO_2$ mixed support is in an amorphous or a poorly crystalline state up to the 873-K calcination temperature. However, formation of crystalline $ZrTiO_4$ compound can be clearly noted from 973 K and above temperatures. Further, the intensity of the lines due to the $ZrTiO_4$ compound increase with the increase in calcination temperature up to 1273 K. Recently, Fung and Wang (19) also reported the formation of the $ZrTiO_4$ compound at 923 K and above temperatures. Noguchi and Mizuno (29) have reported that tetragonal and monoclinic $ZrO_2$ and rutile $TiO_2$ could be formed by the decomposition of $ZrTiO_4$ at higher temperatures. Wu and co-workers (30) also reported the formation of the $TiO_2$ (rutile) phase at higher calcination temperatures. No independent lines due to $TiO_2$ (anatase or rutile) and $ZrO_2$ (monoclinic, tetragonal, or cubic) phases are observed in the present study. The observed high stability of $ZrTiO_4$ compound up to 1273 K calcination temperature (Fig. 1), as well as its formation at lower temperatures, may presumably be due to a different preparation method adopted and the precursor compounds used for the preparation of the mixed oxide support in the present study (22).

XRD patterns of $MoO_3$/$TiO_2$-$ZrO_2$ catalysts containing 2–12 wt% $MoO_3$ and calcined at different temperatures from 773 to 1073 K are shown in Figs. 2–5, respectively. As can be noted from Fig. 2, there are no lines due to $MoO_3$ or a compound between molybdena and titania-zirconia up to
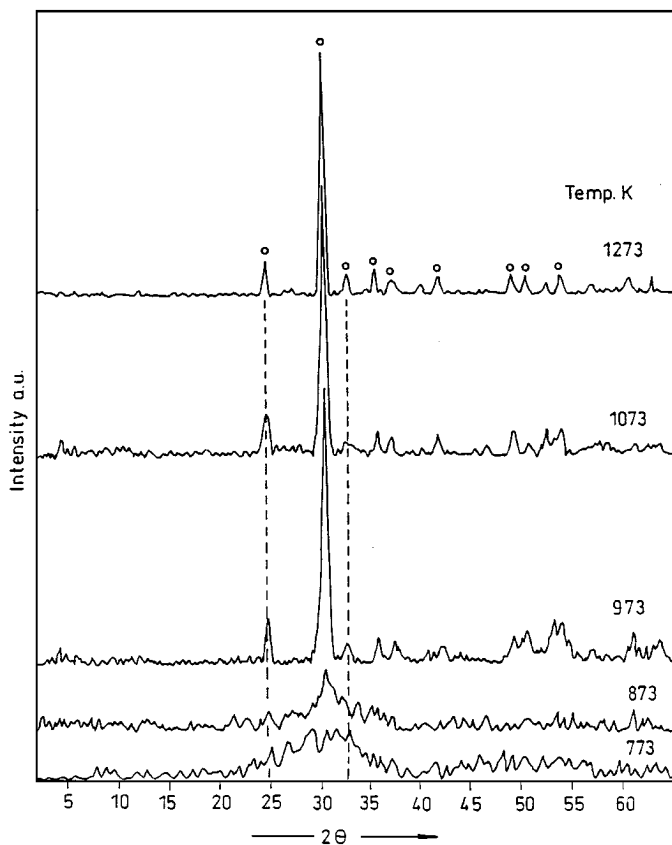
**FIG. 1.** X-ray diffraction patterns of TiO$_2$-ZrO$_2$ calcined at various temperatures: (○) lines due to ZrTiO$_4$.



**FIG. 2.** X-ray diffraction patterns of MoO$_3$/TiO$_2$-ZrO$_2$ catalysts calcined at 773 K: (○) lines due to ZrTiO$_4$; (●) lines due to ZrMo$_2$O$_8$.

It appears from this figure that the ZrMo$_2$O$_8$ compound is formed at the expense of the ZrTiO$_4$ phase. Another interesting point to note from this figure is that the quantity of MoO$_3$ is also an equally important factor for formation of the ZrMo$_2$O$_8$ compound, in addition to the calcination

a loading of 8%, except broad background diffraction lines due to the amorphous ZrTiO$_4$ phase. The XRD results thus indicate that molybdenum oxide is in a highly dispersed state on the mixed oxide support up to 8% loading. This observation is further supported by oxygen uptake measurements as described in the later paragraphs. However, in the case of 12% MoO$_3$/TiO$_2$-ZrO$_2$ catalyst the formation of both ZrTiO$_4$ and ZrMo$_2$O$_8$ compounds can be seen. It is well known in the literature that for molybdena contents of less than monolayer coverage the active component will normally be present as a two-dimensional molybdenum oxide overlayer on the oxide support. Quantities in excess of monolayer coverage will have microcrystalline MoO$_3$ particles present on the catalyst surface in addition to the surface molybdenum oxide overlayer (31). However, it is interesting to note from Fig. 2 that the formation of ZrMo$_2$O$_8$ compound even at 773 K, which is expected to be formed at the expense of MoO$_3$ on TiO$_2$-ZrO$_2$ surface (32).

On increase of the calcination temperature from 773 to 873 K the formation of ZrMo$_2$O$_8$ was noted even at 4% loading (Fig. 3). With an increase in the quantity of MoO$_3$, a gradual increase in the intensity of the ZrMo$_2$O$_8$ lines and at the same time a gradual decrease in the intensity of lines due to the ZrTiO$_4$ phase can also be noted from this figure.
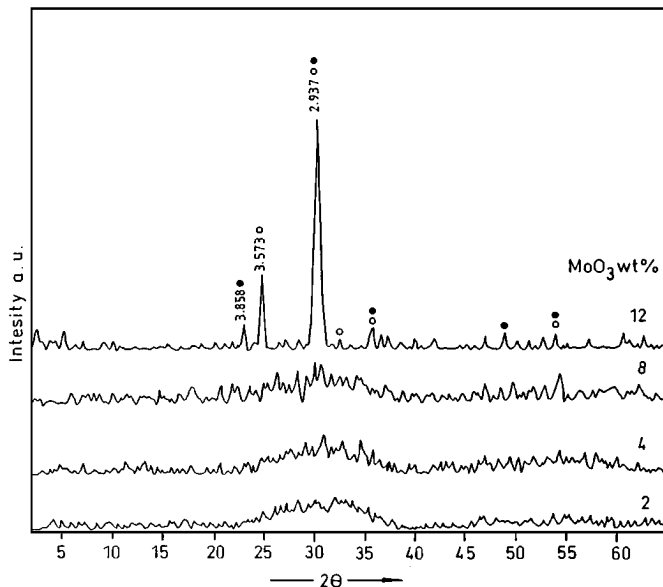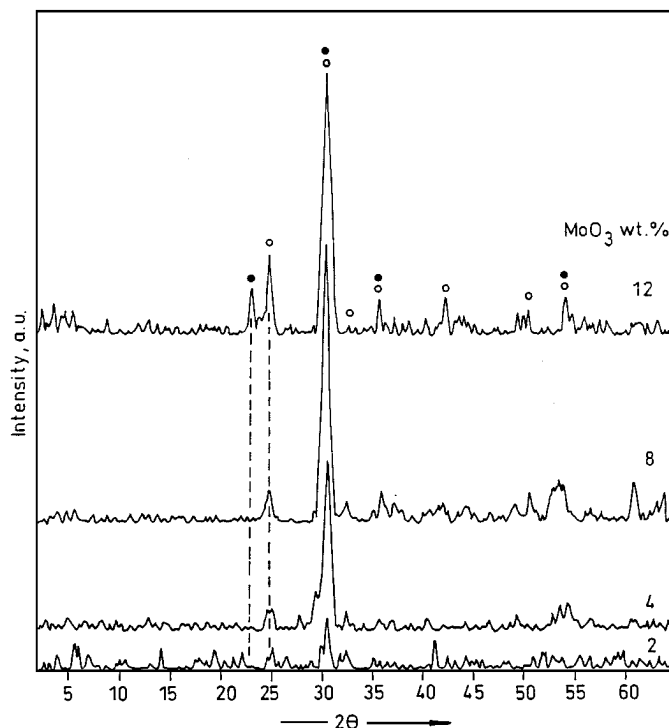


**FIG. 3.** X-ray diffraction patterns of MoO$_3$/TiO$_2$-ZrO$_2$ catalysts calcined at 873 K: Symbols as in Fig. 2.

temperature. Upon further increase of calcination temperature from 873 to 973 K the formation of $ZrMo_2O_8$ was observed at 2% $MoO_3$ (Fig. 4). Here, too, the intensity of lines due to $ZrMo_2O_8$ are found to increase with the increase in molybdena content and at the same time a gradual decrease in the intensity of peaks due to the $ZrTiO_4$ phase can also be seen. XRD lines due to both anatase and rutile forms of titania are also observed at this calcination temperature (Fig. 4). With the increase of molybdena loading the intensity of lines due to the anatase phase are found to decrease while the rutile lines are increased. On further increase of calcination temperature from 973 to 1073 K a further improvement in the intensity of lines due to the $ZrMo_2O_8$ compound are noted (Fig. 5). Here again with increase of the molybdena content from 2 to 12% evidently showed a positive influence on the intensity of lines due to $ZrMo_2O_8$ compound and the $TiO_2$ rutile phase, while it showed a negative consequence on the lines of $ZrTiO_4$ and $TiO_2$ anatase phase.

The XRD observations described above give interesting information about the reactivity of molybdena towards the $ZrTiO_4$ compound. It appears from these results that the
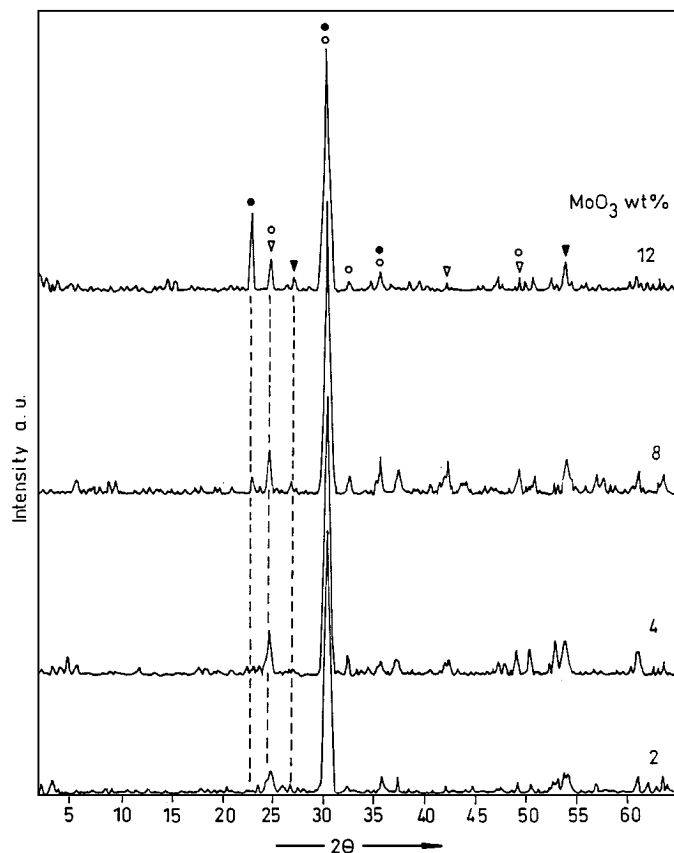


**FIG. 4.** X-ray diffraction patterns of $MoO_3/TiO_2$-$ZrO_2$ catalysts calcined at 973 K: ($\nabla$) lines due to $TiO_2$ anatase; ($\blacktriangledown$) lines due to $TiO_2$ rutile; other symbols as in Fig. 2.
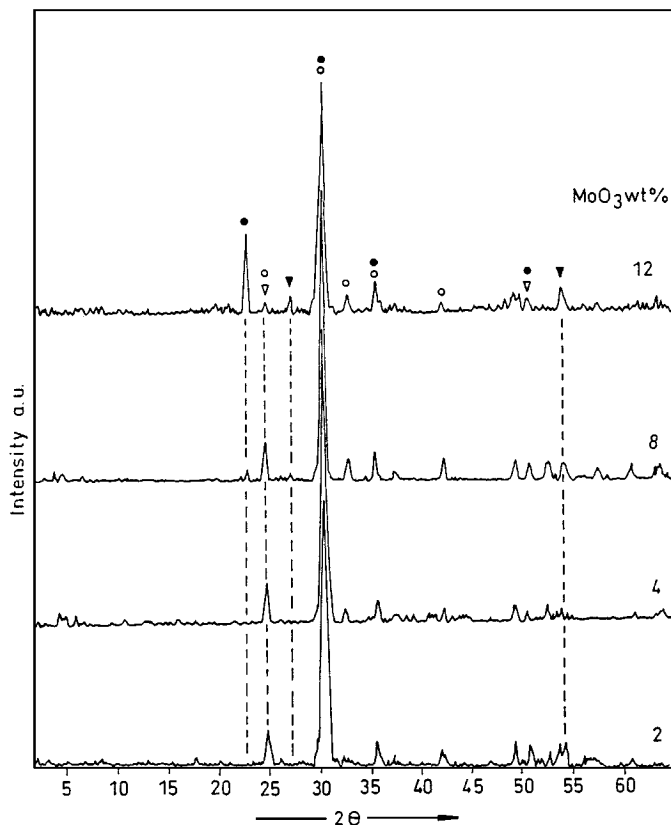


**FIG. 5.** X-ray diffraction patterns of $MoO_3/TiO_2$-$ZrO_2$ catalysts calcined at 1073 K: Symbols as in Fig. 4.

molybdena reacts preferably with the $ZrO_2$ portion of the $ZrTiO_4$ compound to form the $ZrMo_2O_8$ phase, thus liberating the $TiO_2$. The portion of $TiO_2$ released from the $ZrTiO_4$ compound appears as the crystalline anatase or rutile phase as shown in Eq. [1]:

$$ZrTiO_4 + 2MoO_3 \rightarrow ZrMo_2O_8 + TiO_2 \text{ (anatase and rutile)}.$$

$$[1]$$
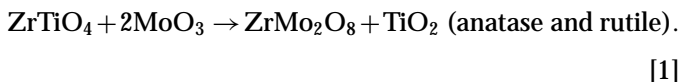
We recently (22) reported an analogous reaction between $V_2O_5$ and $ZrTiO_4$ as shown in Eq. [2]:

$$ZrTiO_4 + V_2O_5 \rightarrow ZrV_2O_7 + TiO_2 \text{ (rutile)}. \quad [2]$$
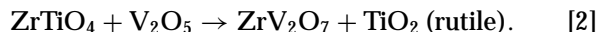
The peaks due to the $ZrV_2O_7$ compound were noted from 973 K and above temperatures when $V_2O_5$ was impregnated on $TiO_2$-$ZrO_2$ mixed oxide (22). It is worthwhile to mention here that in the case of the $V_2O_5$ system $TiO_2$ (rutile) peaks were observed, along with the $ZrV_2O_7$ compound formation. However, in the present molybdena system both rutile and anatase peaks are observed with varying intensities, depending on the quantity of $MoO_3$ present and calcination temperature employed. This study shows that $MoO_3$ is more reactive to form a compound with $ZrO_2$ and less active

to the phase transformation of titania anatase-into-rutile when compared to $V_2O_5$. It is widely established that highly dispersed vanadia on $TiO_2$ support accelerates the so-called anatase-into-rutile phase transformation by lowering the activation temperature of this phenomena (33–35). As we pointed out earlier, both $V_2O_5$ and $MoO_3$ exhibit layer structures and a fit of various crystallographic planes of these oxides to the titania faces is also an established fact (17, 33–37). However, these two oxides appear to behave differently when impregnated on the surface of titania-zirconia mixed oxide and thermally treated at different temperatures.

The FTIR spectra of $TiO_2$-$ZrO_2$ mixed oxide support calcined at various temperatures from 773 to 1273 K are shown in Fig. 6. This figure clearly reveals the presence of two absorption bands at around 740 and 830 cm$^{-1}$ from 973 K and above calcination temperatures. As in XRD (Fig. 1), the intensity of these bands increases with an increase in the calcination temperature. The IR spectra of $MoO_3$/$TiO_2$-$ZrO_2$ catalysts calcined at 773 and 1073 K are shown in
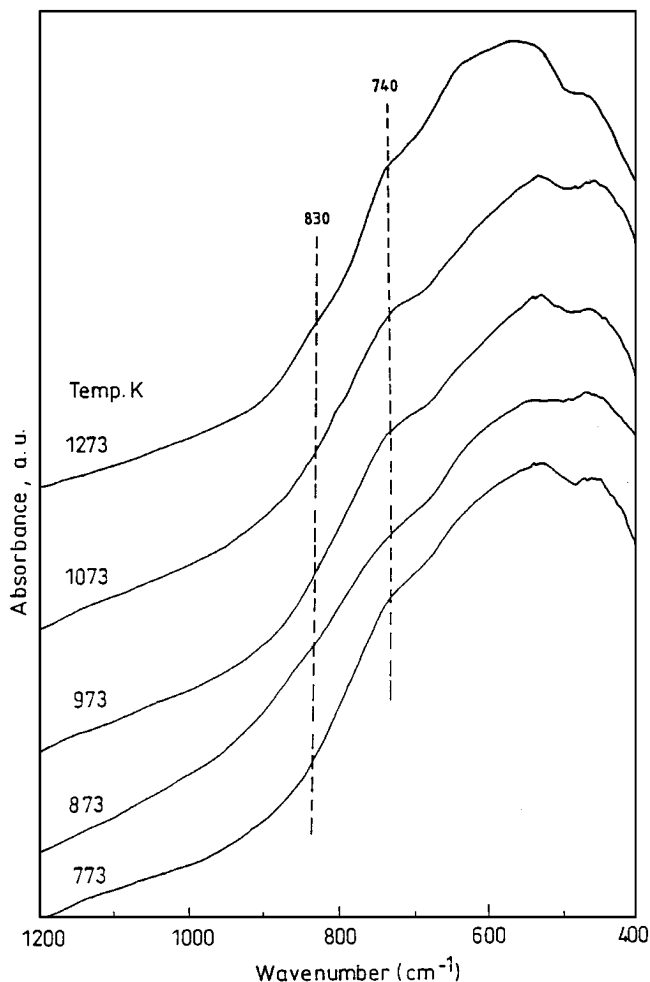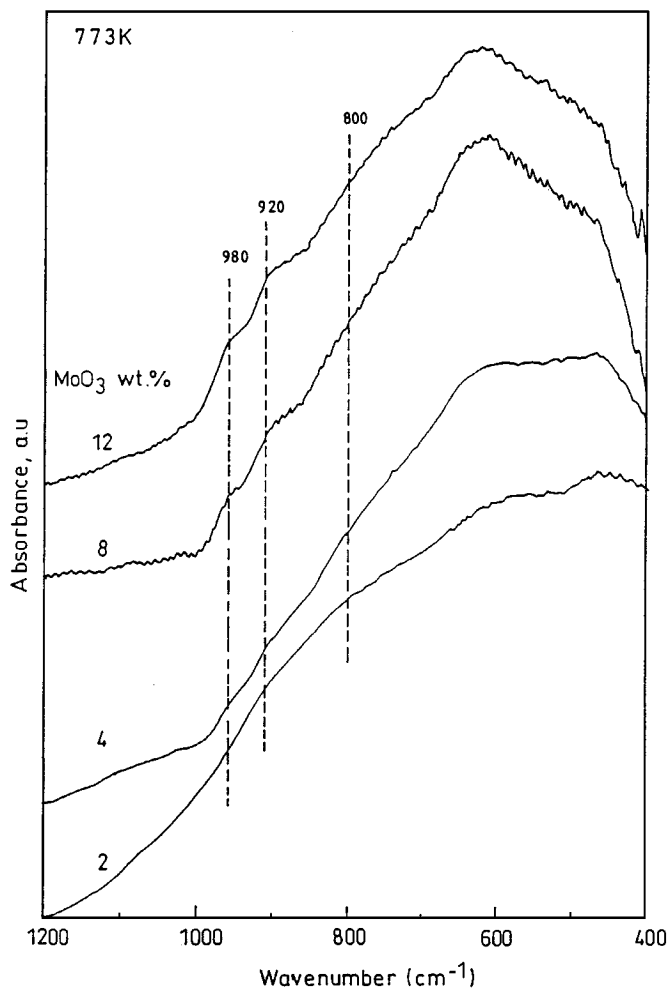


FIG. 7. FTIR spectra of $MoO_3$/$TiO_2$-$ZrO_2$ catalysts calcined at 773 K.

Figs. 7 and 8, respectively. Similar spectra were obtained for 873 and 973 K calcined samples. Generally, the IR band of Mo=O in crystalline $MoO_3$ appears at 1000 cm$^{-1}$ due to the stretching vibration mode. Frausen et al. (32) reported the formation of the $ZrMo_2O_8$ compound by heating $ZrO_2$ with $MoO_3$ together at 820 K, which showed the IR bands at 980, 920, and 800 cm$^{-1}$. A close look at Figs. 6–8 reveals that there is substantial evidence for the formation of both $ZrTiO_4$ and $ZrMo_2O_8$ compounds whose concentration is also dependent on the quantity of $MoO_3$ present in the sample and the calcination temperature employed. An interesting observation to note from these figures is that, irrespective of the calcination temperature and molybdena content, no characteristic bands due to crystalline $MoO_3$ are observed. There is also a clear indication of high dispersion of $MoO_3$ on $TiO_2$-$ZrO_2$ mixed oxide at 773 K. The anatase and rutile phases of titania exhibit strong absorption bands in the region of 850–650 and 800–650 cm$^{-1}$, respectively. The presence of these phases, especially at 1073 K, can also be noted from FTIR, in line with XRD observations. Thus,
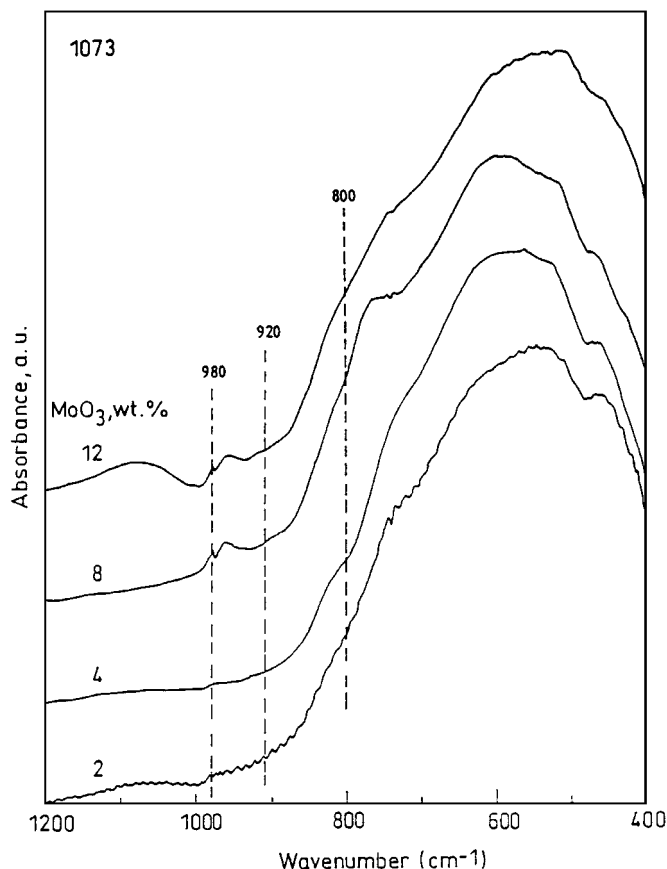


FIG. 6. FTIR spectra of $TiO_2$-$ZrO_2$ calcined at various temperatures.

**FIG. 8.** FTIR spectra of $MoO_3/TiO_2$-$ZrO_2$ catalysts calcined at 1073 K.

FTIR results perfectly agree with the observations made from the XRD measurements.

The BET surface area and oxygen uptake capacities of $MoO_3/TiO_2$-$ZrO_2$ catalysts calcined at various temperatures are shown in Table 1. This table also lists the dispersion of Mo-oxide on the support derived from oxygen uptake measurements. Depending on the calcination temperature the pure $TiO_2$-$ZrO_2$ support alone was also found to chemisorb some small amount of $O_2$ under the experimental conditions employed in this study. Therefore, the contribution of the support alone was subtracted from the results. A considerable decrease in the specific surface area of catalysts depending on the calcination temperature and $MoO_3$ loading can be noted from Table 1. The decrease in specific surface area with the increase in calcination temperature is a general phenomenon and is expected to be due to sintering of the samples at higher temperatures. Similarly, the decrease in the specific surface area with the increase in $MoO_3$ loading at a given calcination temperature is presumably due to the blocking of pores of the support by the dispersed molybdena (31).

In general, the oxygen uptake increases with the increase in molybdena loading, irrespective of the calcination temperature. However, the numerical values of $O_2$ uptakes vary

appreciably and are maximum in the case of catalysts calcined at 773 K and minimum at 1073 K. Among all samples, the 8% catalyst calcined at 773 K shows maximum dispersion of molybdenum oxide on the $TiO_2$-$ZrO_2$ mixed oxide support. Increasing the calcination temperature also results in a decrease in the dispersion of molybdena, especially in the case of catalysts calcined at 1073 K. The decrease in the dispersion with the increase in calcination temperature, as well as $MoO_3$ loading, are primarily due to the $ZrMo_2O_8$ compound formation. The quantity of this compound is highly dependent on the concentration of $MoO_3$ loading and calcination temperature. Thus, the $O_2$ uptake results are in line with XRD and FTIR observations. The oxygen chemisorption at low or high temperatures have been widely used to investigate the supported molybdena catalysts. Several attempts have been made in the literature to correlate the oxygen uptake capacity of the catalysts with their catalytic properties (6,38,39). There is no universal agreement regarding the property measured by oxygen uptake, however, it is generally accepted that the dispersion of molybdena oxide or sulfide can be made by this simple and quick method (38,40). These details are not important in the present context.

**TABLE 1**

**Oxygen Uptake and BET Surface Area Results on $MoO_3/TiO_2$-$ZrO_2$ Catalysts Calcined at Various Temperatures from 773 to 1073 K**

| $MoO_3$ (wt.%)[a] | Surface area ($m^2 g^{-1}$) | $O_2$ uptake[b] ($\mu$ mole $g^{-1}$) | Dispersion[c] (%) |
|---|---|---|---|
| **773 K** | | | |
| 2 | 128.7 | 55.5 | 80 |
| 4 | 125.3 | 124.9 | 89 |
| 8 | 96.5 | 275.1 | 99 |
| 12 | 75.9 | 393.0 | 94 |
| **873 K** | | | |
| 2 | 107.8 | 48.6 | 70 |
| 4 | 89.1 | 105.5 | 76 |
| 8 | 69.7 | 222.3 | 80 |
| 12 | 57.4 | 342.0 | 82 |
| **973 K** | | | |
| 2 | 73.3 | 45.1 | 65 |
| 4 | 65.0 | 97.2 | 70 |
| 8 | 33.5 | 205.6 | 74 |
| 12 | 26.6 | 298.0 | 70 |
| **1073 K** | | | |
| 2 | 30.5 | 38.9 | 56 |
| 4 | 27.6 | 83.4 | 60 |
| 8 | 22.3 | 180.6 | 65 |
| 12 | 15.7 | 208.4 | 50 |

[a] The balance is $TiO_2$-$ZrO_2$.
[b] The contribution of $TiO_2$-$ZrO_2$ support calcined at various temperatures, 6.2 (773 K), 3.8 (873 K), 2.2 (973 K), and 0.0 $\mu$ mole $g^{-1}$ (1073 K), respectively, was subtracted from the results.
[c] Dispersion = Fraction of molybdenum atoms at the surface, assuming $O_{ads}/Mo_{surf} = 1$.

## CONCLUSIONS

The following conclusions can be drawn from this study: (1) The $TiO_2$-$ZrO_2$ mixed oxide support when calcined at 773 K is in X-ray amorphous state and exhibits a high specific surface area. The amorphous $TiO_2$-$ZrO_2$ gets converted into $ZrTiO_4$ compound beyond 873 K calcination temperature and this compound is thermally quite stable even up to 1273 K. (2) Calcination of $MoO_3$/$TiO_2$-$ZrO_2$ catalysts at 773 K result in a highly dispersed molybdenum oxide phase on the support surface up to 8% $MoO_3$. Molybdena concentration in excess of 8% results in the formation of $ZrMo_2O_8$ compound. (3) $MoO_3$ selectively interacts with $ZrO_2$ portion of $TiO_2$-$ZrO_2$ mixed oxide and readily forms the $ZrMo_2O_8$ compound with the liberation of $TiO_2$. The $ZrMo_2O_8$ compound is highly sensitive to the concentration of $MoO_3$ and calcination temperature. The liberated $TiO_2$ appears in the form of both anatase and rutile with varying intensities. The intensity of rutile increases with increase in $MoO_3$ content and calcination temperature while the anatase phase decreases. (4) The $MoO_3$ in $TiO_2$-$ZrO_2$ mixed oxide appears to be less reactive than $V_2O_5$ towards phase transformation of $TiO_2$ anatase-into-rutile (37).

Finally, further studies are required in order to understand fully the microscopic mechanism of the selective interaction of $MoO_3$ with $ZrO_2$ portion of $TiO_2$-$ZrO_2$ mixed oxide support resulting in the formation of $ZrMo_2O_8$.

## ACKNOWLEDGMENT

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